Tetranuclear CuII2DyIII2 coordination cluster as Suzuki (C–C) coupling reaction promoter

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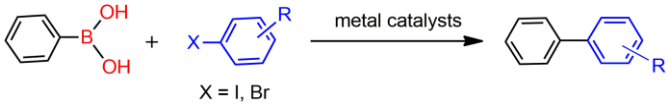
The air stable and high yielding tetranuclear coordination cluster $[Cu^{II}_2Dy^{III}_2L_4(NO_3)_2(CH_3CN)_2]\cdot 2(CH_3CN)$ promotes the Suzuki coupling reaction of phenylboronic acid with substituted aryl halides in environmentally benign conditions.

Long term research is required to obtain synthetic control in combining 3d and 4f centres with organic ligands as well understanding the influence of each centre on the studied property, however this methodology has yield entities with exceptional magnetic[1] or luminescent behaviour.[2] The development of earth-abundant metal-based catalytic methodologies to replace existing practices that use noble and rare elements is a key target in modern science.[3] In this direction, 3d/4f in situ[4–6] or well characterised coordination clusters have recently emerged as sustainable catalytic platforms with advantages in their ease synthesis, good abundance (in spite of belonging to the so-called rare earths) and low cost.[7] Our group has established the efficacy of a series of tetranuclear $[M^{II}_2Ln^{III}_2L_4(X)_2(solv)_2]$ (M = Ni, Co, Cu, Zn, X = Cl, NO_3, Ln = Y, Dy, Gd) for domino-electro cyclization and Lewis acid reactions,[8–11] whereas other groups have, successfully, used them in redox,[12–14] co-polymerization[15] and carbon dioxide fixation reactions.[16,17]

The metal-promoted Suzuki-Miyaura coupling includes organoboron derivatives and carbon electrophiles, and represents a valuable procedure for a C-C bond formation (Scheme 1).[18] This synthetic protocol uses commercially available boron reactants, which are relatively stable, non-toxic and can be easily functionalized. The initial reports involved noble and expensive Pd-based catalysts, however several methodologies, based on earth-abundant, low cost, first row transition elements such as Fe,[19] Co[20], Ni[21] and Cu[22] have been identified. In the case of the Cu promoted catalysis,[23,24] the high loadings required to achieve the C-C bond-formation in high yields is considered a significant drawback.



Scheme 1. A representative example of the Suzuki C-C coupling reaction

In our quest to investigate and expand the applicability of the $[M^{II}_2Ln^{III}_2L_4]$ 3d/4f catalytic species further and given the successful use of Cu^{II} based compounds in the Suzuki-Miyaura reaction, we synthesised the compound $[Cu^{II}_2Dy^{III}_2L_4(NO_3)_2(CH_3CN)_2]\cdot 2(CH_3CN)$, **1**·2($CH_3CN$), where H_2L is the Schiff base ligand (*E*)-2-(2-hydroxy-3-methoxybenzylidene-amino)phenol. Compound **1** is synthesized in two high-yielding steps (overall yield 93%), under ambient conditions, using commercially available starting materials, from the reaction of $Cu(NO_3)_2\cdot 3H_2O$, $Dy(NO_3)_3\cdot 6H_2O$, H_2L and Et_3N in MeCN (20 mL) in a molar ratio (2:4:4:9). After mixing, the resulting solution was filtered and greenish crystals of **1**·2(CH_3CN) were obtained in 3 days from the mother liquor and collected by filtration, washed with Et_2O, and dried in air. Compound **1** crystallizes in the orthorhombic space group *P*bca. Its core topology is of the well-known tetranuclear defect dicubane or butterfly type (Figure 1). The Cu^{II} ions are in the central "body" positions and the Dy^{III} ions at the "wingtip" positions with a separation of 3.4105(9) Å, whereas the Cu-Cu distance is 3.411 Å. The coordination environment of both metals is almost saturated; five out of six and six out of eight coordination sites of the Cu^{II} and Dy^{III} centres respectively are occupied by the ligand. The final coordination site on the Cu^{II} is taken by a solvent MeCN molecule and the remaining two sites on Dy^{III} are occupied by two oxygen atoms from a chelating nitrate anion. This compound is isoskeletal to the previously reported tetranuclear compounds and more specifically to $[Cu^{II}_2Y^{III}_2L_4(NO_3)_2(DMF)_2]$, which was found to be an efficient cooperative catalyst in a Michael addition reaction.[8] Thermal studies under N_2 atmosphere (Fig S1) identify partial loss of the solvent molecules (9.83%) and that compound **1** is stable up to 250°C. At this

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point the framework collapses to yield the corresponding $Cu^{II}_2Dy^{III}_2O_5$ residue (calculated 31.20%, found 31.01%). To further confirm the identity of compound **1** in solution we recorded a UV-Vis spectrum in CH_3CN. This revealed a broad peak (500 to 700 nm), characteristic of Cu^{II} in this ligation (Fig S2). Preliminary magnetic studies identify the paramagnetic character of compound **1** and that Cu centres are in oxidation state II.

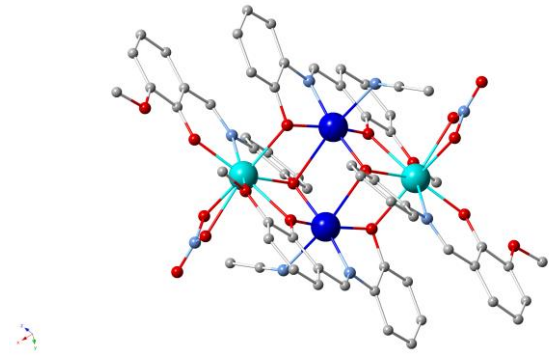
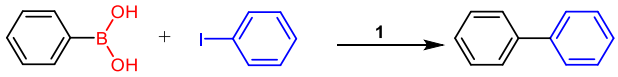


Figure 1. The molecular structure of compound **1** in the crystal. Color codes. Cu^{II} (Dark Blue), Dy^{III} (cyan), Oxygen (red), Nitrogen, (light blue), Carbon (grey). H – atoms are omitted for clarity.

With the catalyst in hand, we chose phenylboronic acid and iodobenzene as model substrates, and attempted to identify environmentally friendly solvents[25] to perform the reaction (Table 1). The completion of the reaction was monitored by TLC. Two experiments in absence of compound **1** were performed as blank to exclude the release of Pd nanoparticles from the magnetic stirrer. After 24 h, compound **1** showed higher activity in the mixture DME : water (1:1) ratio with 89% yield of the desired 1,1'-biphenyl product (Table 1, entry 4). The reaction was performed in other solvents such as water, ethanol, DME (dimethoxyethane), DMF (dimethylformide), DMF : water (1 : 1), THF (tetrahydrofuran), and THF : water (1:1), however the corresponding compound was obtained in lower yields. Therefore, the mixture DME : water (1 : 1) was chosen as the solvent for the subsequent experiments..

Table 1. Influence of the solvent[a]



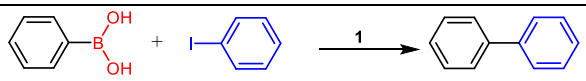
2a 3a 4aa

Entry	Solvent	Yield[b]
1	water	10
2	Ethanol	12
3	DME	46
4	**DME : water(1:1)**	**89**
5	DMF	66
6	DMF : water(1:1)	79
7	THF	36
8	THF : water(1:1)	48

[a] Iodobenzene (1.0 mmol), phenylboronic acid (1.1 mmol), PPh_3 (2.0 mol%), K_2CO_3 (5.0 mmol), Cu_2Dy_2 (5.0 mol%), 80 °C. [b] Isolated yield.

Further, the effect of a base on the reaction performance was studied using different bases such as K_2CO_3, KOH, Na_2CO_3, NaOH, Et_3N, Cs_2CO_3 and KO^{t}Bu in a mixture of DME and water solvent (Fig. S2). We identified that the K_2CO_3 is the desirable base for the reaction with higher product yield for this reaction. In the absence of catalyst, the coupling product is formed at very low yielding (>2%) using K_2CO_3 as the base. Therefore, we may envisage that the presence of the base is essential to activate boronic acid via enhancing the polarization of the organic ligand and thus facilitate transmetallation. The next step was to use different loadings of the catalyst. As shown in Table 2, the initial experiment of 5.0 mol% is the optimum condition.

Table 2. Optimization experiments for the coupling reaction of phenyl boronic acid and iodobenzene catalysed by compound **1**.[a]



2a 3a 4aa

Entry	Catalyst (mol %)	Yield[b]
1	1	48
2	2	56
3	**5**	**89**
4	10	72
5	20	69

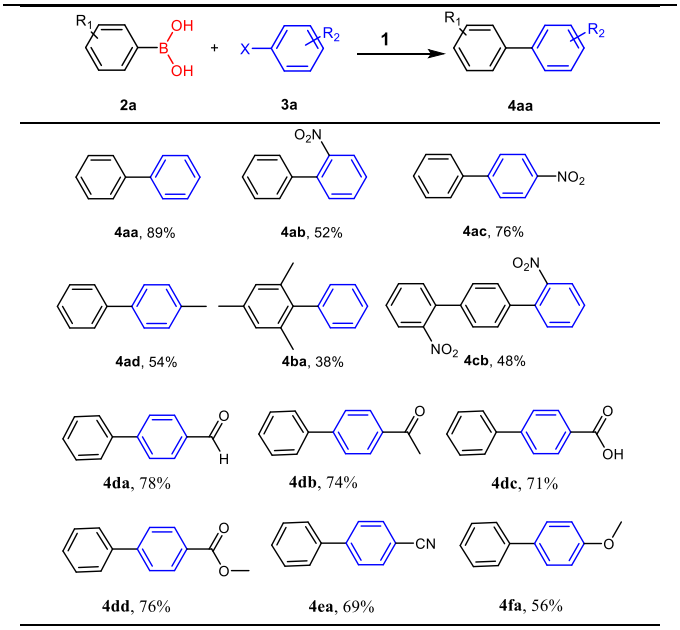
[a]Iodobenzene (1.0 mmol), phenylboronic acid (1.1mmol), PPh_3 (2.0 mmol), K_2CO_3 (5.0 mmol) DME:water (1:1), 80 °C. [b] Isolated yield.

Then, we investigated the influence of the temperature on the coupling reaction between phenylboronic acid and iodobenzene in a range of temperature (0° C – 120°C). Control experiments showed that **1** can give good conversion at 80° C but is inactive at temperatures lower than 40°C (Fig S3). At 100 and 120 °C, the catalyst affords the corresponding compound at lower yields, therefore we concluded that the temperature of 80 °C was optimum. Moreover, experiments in the presence of Cu salts under similar catalytic conditions yielded the expected product in significantly higher loadings when compared with **1**. For example, various Cu(II) salts (Table S1) show up to 33% conversion, whereas the use of $Dy(NO_3)_3$ does not promote the organic transformation. The use of Cu(I) salts yields the corresponding product in 40% yield, which is slightly higher than for the Cu(II) salts, whilst the in situ combination of $Cu(NO_3)_2$ / $Dy(NO_3)_3$ / H_2L gave a poor outcome (entry 7, Table S1), showcasing the advantage of the use of the well characterised material.

With the optimal reaction conditions in hand, we then extended the scope of the reaction and performed the coupling reactions between different aryl halides and phenylboronic acid. As a first step, we investigated the influence of the substitution on the aromatic ring of the aryl halide. The reactions with substitution in the *ortho* and *para* position of the aryl halide ($-NO_2$) yielded the corresponding products in moderate to good yields. The electron-withdrawing group ($-NO_2$) of aryl halide enhance the rate of cross-coupling. For example, nitro ($-NO_2$) group at the para position of aromatic aryl

halide furnished the desired product **4ac** with 76% yield (Table 3) and electron-donating group (-CH_3) at para position of aryl halide produced corresponding product **4ad** with 54% yield (Table 3). Furthermore, the reaction with sterically hindered halides with phenylboronic acid afforded **4ba** with 38% yield (Table 3). The slight increase in the yield of **4ac** when compared with that of **4ab** may be attributed to the influence of the strong electron-withdrawing group (NO_2) that results in reductive halogenation of aryl halides.

Table 3. Reaction of phenylboronic acid with different aryl halides



[a]Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), PPh_3 (2.0 mol%), K_2CO_3 (5.0 mmol), Cu_2Dy_2 (5.0 mol%), 80 °C. [b] Isolated yield.

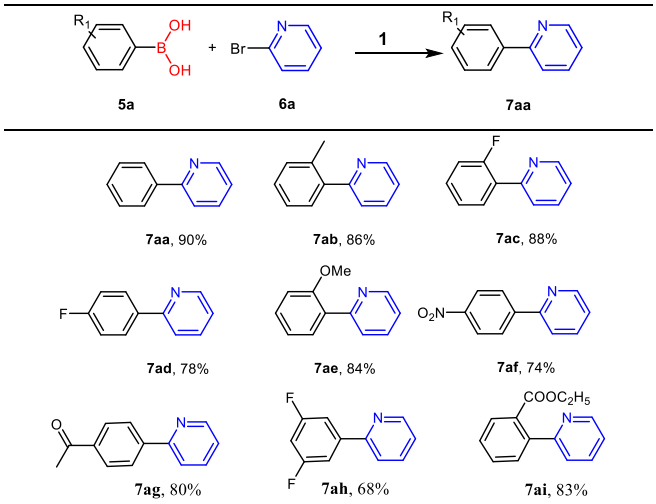
Further, we explored different substituted aryl boronic acid and nitrogen-based heteroaryl halides (2-bromopyridine) using **1** as a precatalyst under same reaction condition and the results are summarized in Table 4. Reactions with both electron-rich and electron-poor aryl boronic acids proceeded smoothly. A quantitative yield of 2-phenylpyridine was obtained in the presence of 5.0 mol% of catalyst **1** at 80 °C in 8 h (Table 4, **7aa**). Electron withdrawing and electron donating group at ortho/para position afforded corresponding products with good yield as compared to the meta-position (Table 4).

Finally, to obtain an initial understanding of the catalyst's role we also tested this coupling reaction with other topological equivalent catalysts, varying the 3d part i.e. $Co^{II}_2Dy_2$, $Ni^{II}_2Dy_2$ and $Zn^{II}_2Dy_2$.[8,26] However, all reactions failed to produce the desired product **4aa** as compared to **1**, thus identifying the suitability and superiority of **1** as catalyst for the Suzuki Coupling reaction under these reaction conditions and justifying our selection of choice.

Conclusions

Extending our studies in exploring the use of 3d/4f coordination clusters as organic transformation promoters, in this work we report, for the first time, the cross coupling activity of compound **1**. The very promising results highlight the richness of the reactivity of the 3d/4f chemistry and its potential applications. The catalytic conversion proceeds under environmentally benign conditions and thus the current methodology has a sustainable character. More experiments are required to fully understand the role of **1** in the present organic transformation and these experiments are under investigation. The present results opens new research avenues for the chemistry of Cu/4f coordination clusters.

Table 4. Reaction of 2-bromopyridine with different phenylboronic acid



[a]Aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), PPh_3 (2.0 mol%), K_2CO_3 (5.0 mmol), Cu_2Dy_2 (5.0 mol%), 80 °C. [b] Isolated yield.

Conflicts of interest

There are no conflicts to declare.

Funding Sources

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